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Development and Optimization of Multi-Functional SCR-DPF Aftertreatment for Heavy-Duty NOx and Soot Emission Reduction

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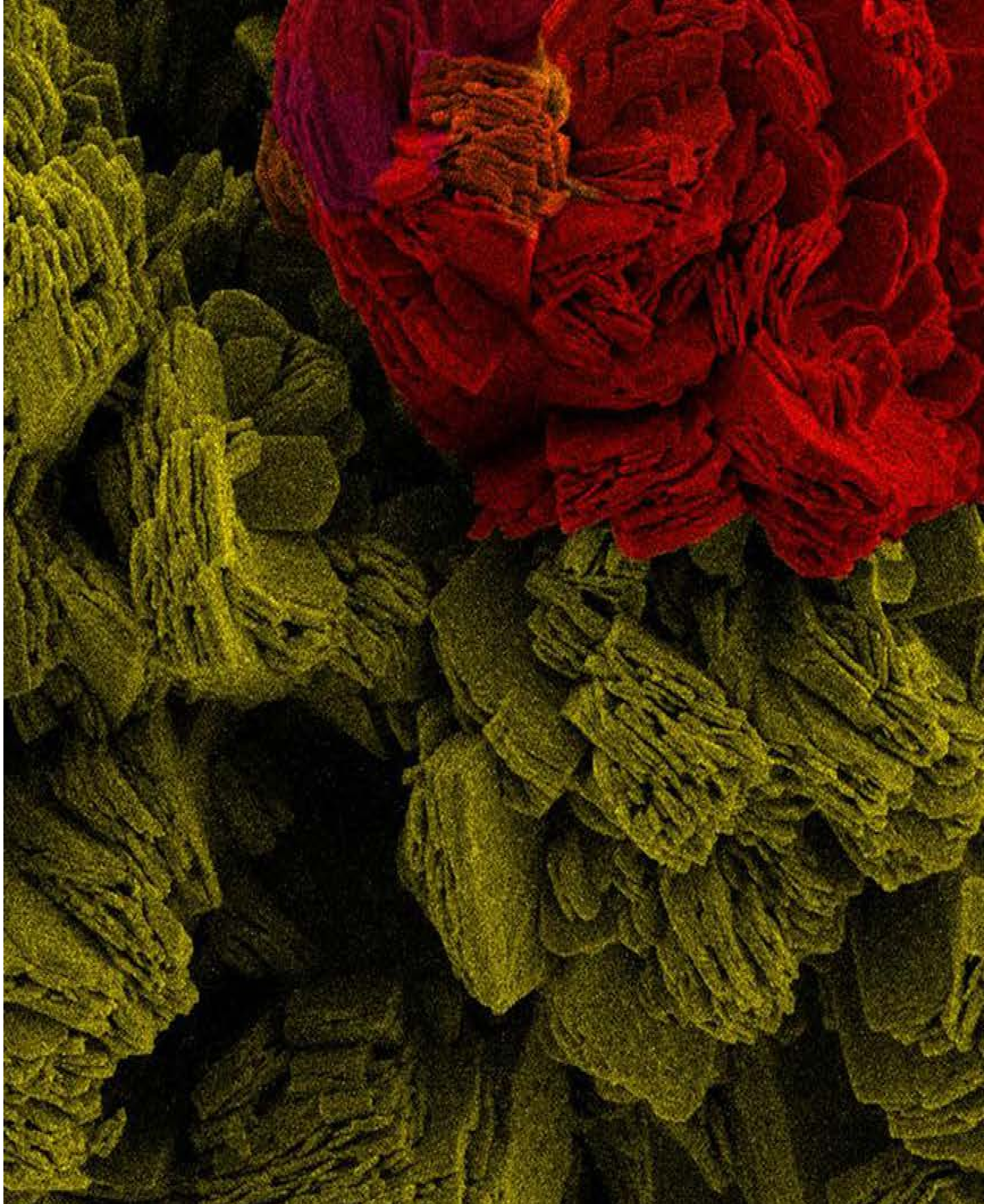


ACE119

Project Overview

Timeline

- 4-yr CRADA
  - Start date – July 2016
  - End date – June 2020
- 68% complete

Barriers

- **B. Lack of cost-effective emission control** for meeting EPA standards for NOx & PM emissions
- **E. Durability** of the emission control system: 435,000 miles (HD)
- **G. Cost of emission control** devices … for heavy duty engines in particular

Budget

- Contract value – $2.7M
  - $1.35M DOE share
  - $1.35M PACCAR share
- Funding received
  - $855K through FY18
  - FY19 – $150K

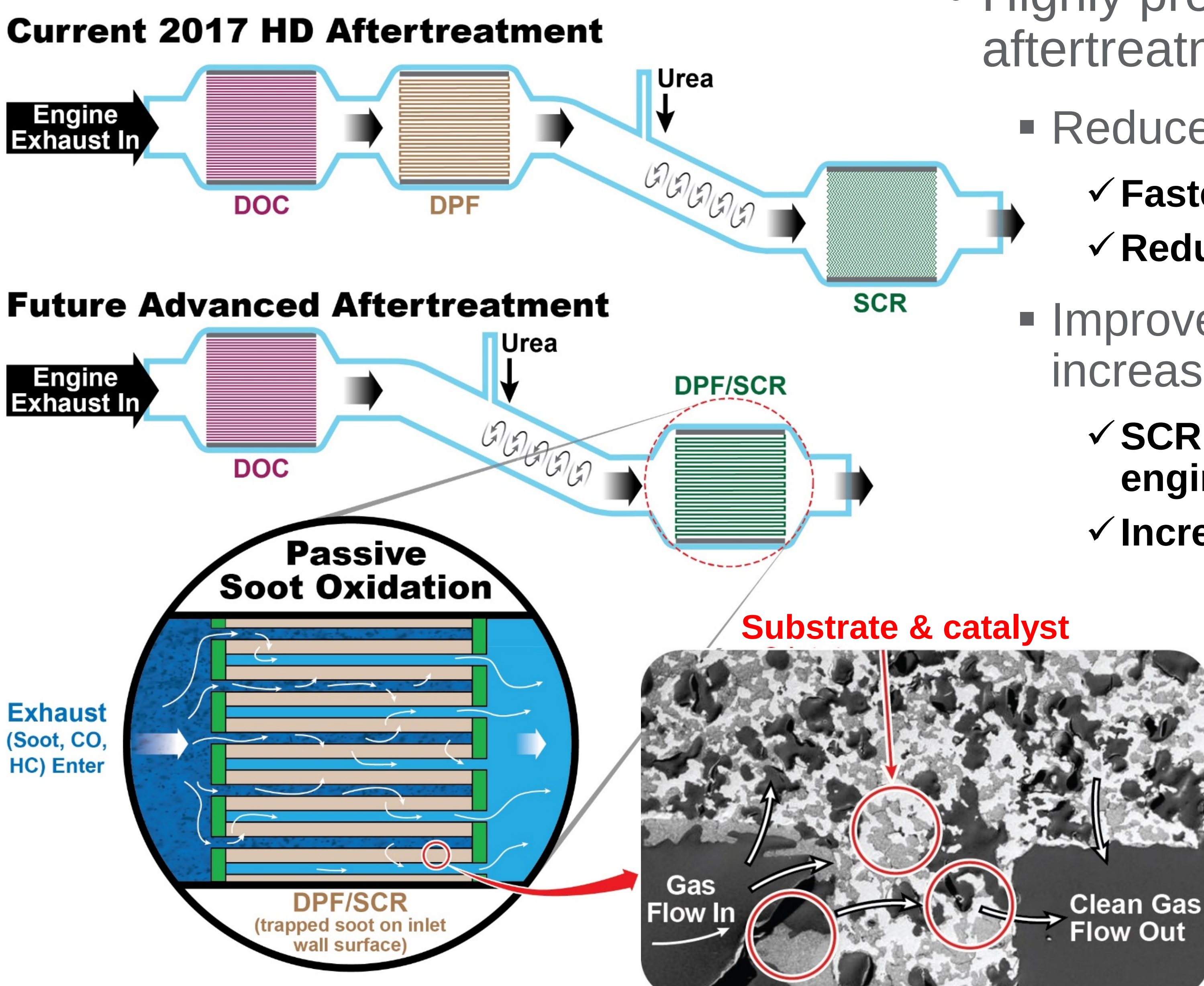
Partners

PACCAR Inc

- CRADA partner

Relevance

Multi-Functional Aftertreatment: SCR-on-DPF for HD



- Highly promising strategy of aftertreatment integration
  - Reduced total thermal mass
    - ✓ **Faster warm-up**
    - ✓ **Reduced cold-start emissions**
  - Improved performance & increased flexibility
    - ✓ **SCR more closely coupled to engine**
    - ✓ **Increased total SCR volume**

✓ **Soot trapped upstream**

✓ **Molecular diffusion to washcoat**

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Relevance

Multi-Functional Aftertreatment: SCR-on-DPF for HD

Challenges to deployment

1. SCR catalyst performance – ***light*** and ***heavy*** duty
   - ➢ Enablers – ultra-high porosity filter development, advanced imaging & coating
2. SCR catalyst durability – ***light*** and ***heavy*** duty
   - ➢ Enablers – small-pore Cu-zeolites, e.g., Cu-SSZ-13 and its derivatives
3. Passive soot oxidation performance (via NO_2) – ***heavy*** duty
   - ➢ Fuel efficient to maximize passive soot oxidation capacity
   - ➢ However, competition for NO_2 arises with incorporation of SCR phase on filter

Passive soot oxidation

$$C\ (soot) + 2\,NO_2 \longrightarrow CO_2 + 2\,NO$$

Significantly compromises soot oxidation

versus

Dominates NO_2 consumption

Fast-SCR

$$2\,NH_3 + NO + NO_2 \longrightarrow 2\,N_2 + 3\,H_2O$$

Approach
The role of the SCO phase

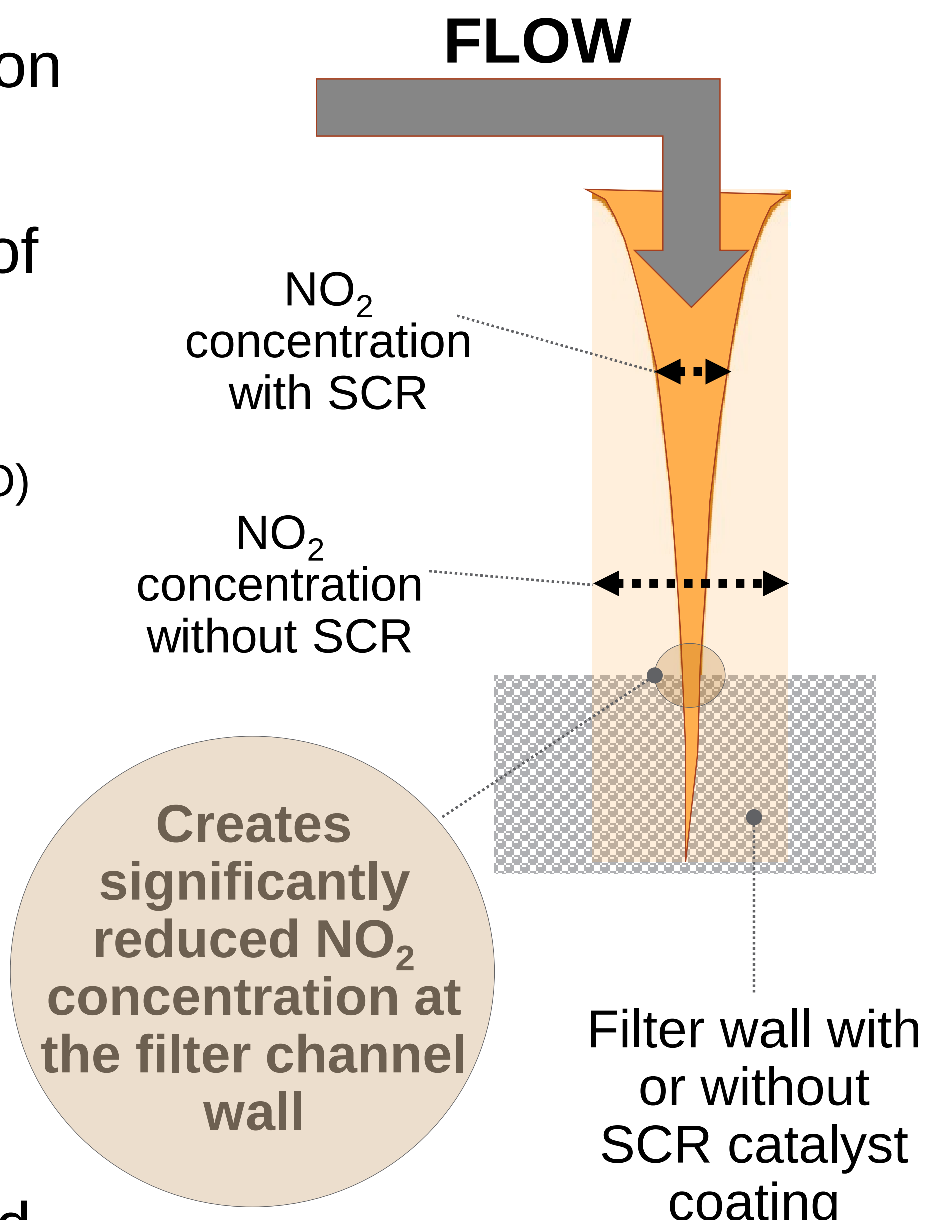
- Goal: Maximize passive soot oxidation activity with SCR catalysis on filter

Approach: Minimize the dependency of fast-SCR catalysis on incoming NO_2
***This is a catalysis challenge*.**

- Incorporate a selective catalytic oxidation (SCO) phase with the SCR catalyst to promote oxidation of NO to NO_2
- This will increase NO_2 at the filter channel wall by ***reducing forward diffusive effects*** on upstream soot

- Role of the SCO phase
  1. Produce local gaseous NO_2, ***or***
  2. Produce active-NO_2 surface intermediate in vicinity to SCR active center(s)
  - Both drive fast SCR "in-situ"

- Mn-based SCO phase being pursued



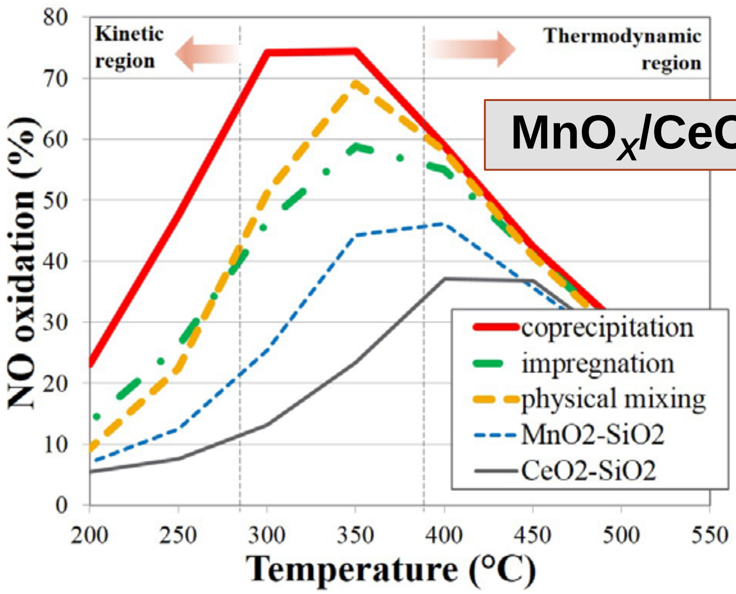
Approach

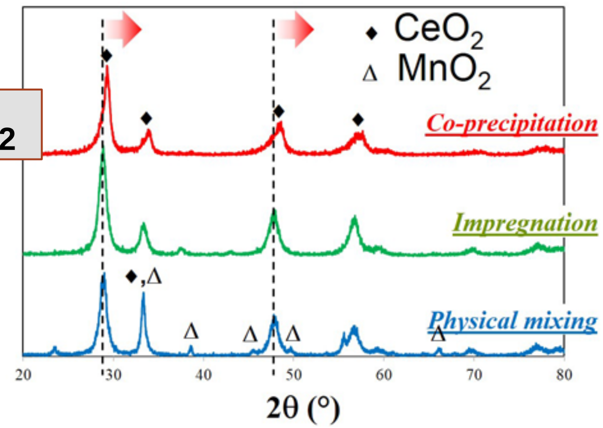
Schedule and Milestones

Date*	Milestone and Go/No-Go Decisions	Status
February 2018	Go/No-Go decision: Identify candidate SCO/SCR binary phase catalyst with improved soot oxidation performance with competing SCR	Complete (PACCAR)
November 2018	Milestone: Optimum DPF and integration strategy developed	Complete
November 2018	Milestone: Begin of increased scale testing	Complete
February 2019	Milestone: Identify SCO-SCR catalyst for full-scale SCRF production	On-going
May 2019	Milestone: SCRF single wall model complete	On-track

Accomplishments

SCO phase preparation identified that maximized Mn-support interaction with enhanced activity





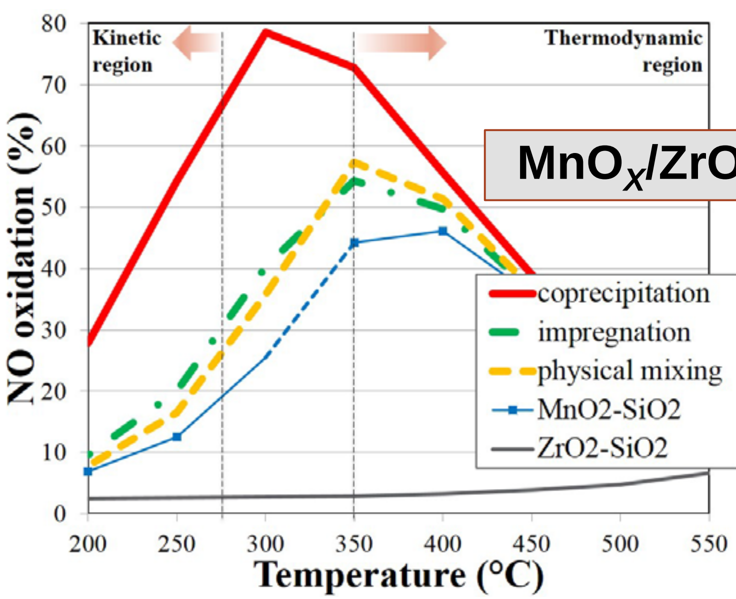
Co-precipitation

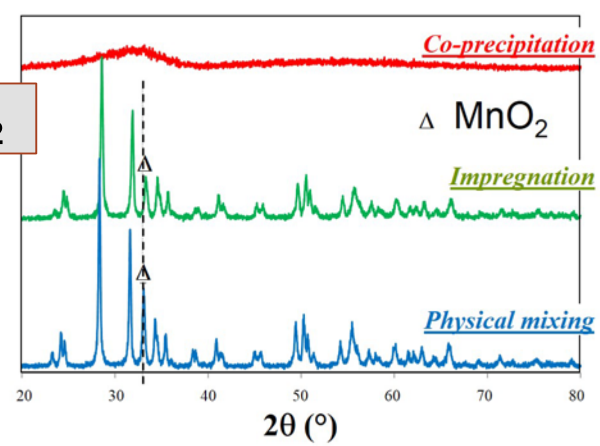
- Suppression of MnO_2 diffraction
- Shift in CeO_2 diffraction
- High MnO_2 dispersion in solid solution.

30 wt% MnO_2
70 wt % CeO_2 or ZrO_2

High dispersion achieved by co-precipitation exhibits superior activity attributed to interface site of MnO_2 and support.

- Focus = ZrO_2 (durability)

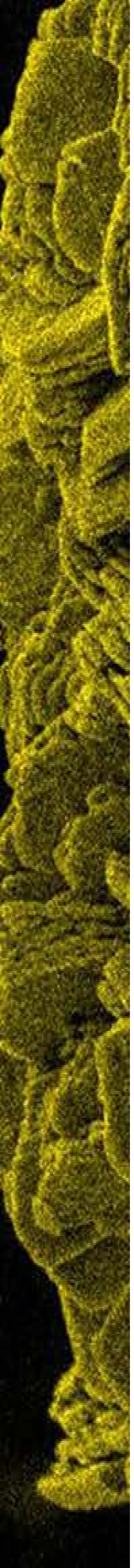




Co-precipitation

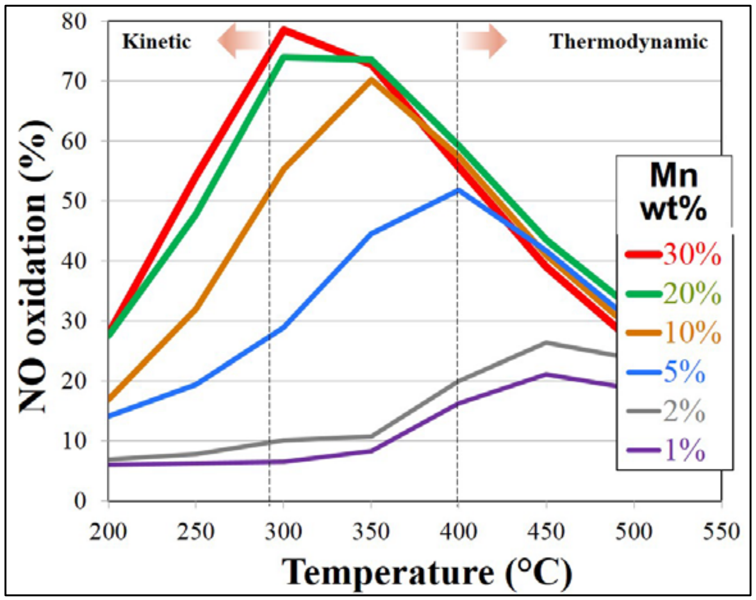
- Saturates solid solution forming high amorphous coverage.
- Activity *much* higher that the sum of each component

Conditions:
320 ppm NO, 14% O_2, 2.5% H_2O, Balance of N_2, SV=300 L/g-hr



Accomplishments

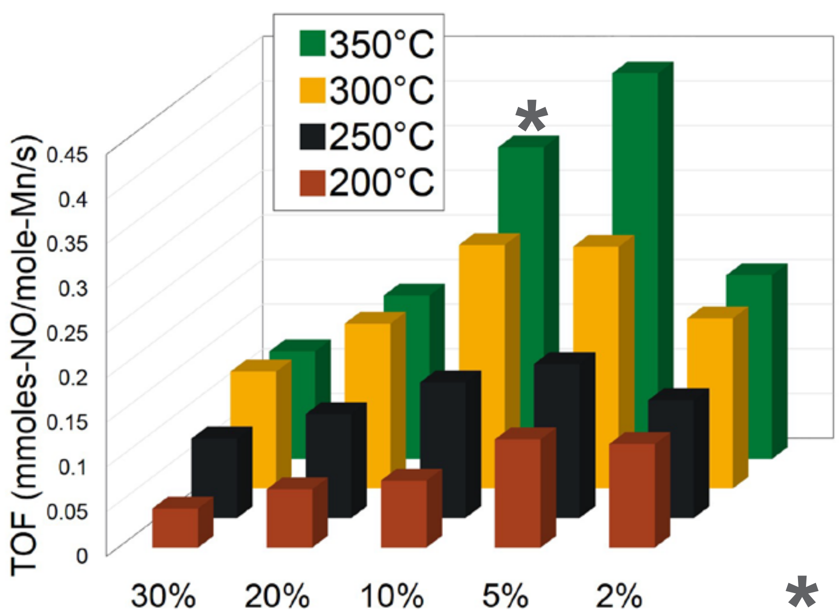
An optimum SCO phase chemistry is developed for high activity & durability: MnO_X-ZrO_2



10 wt% MnO_2 optimum loading on ZrO_2 for catalyst development

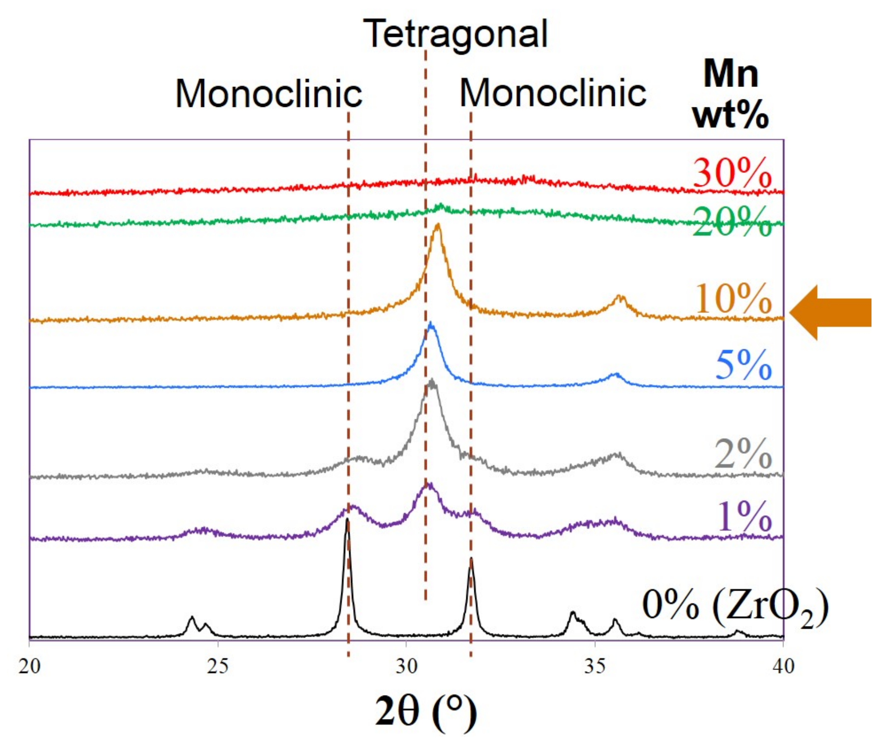
- Significant increased activity >2 wt%
- Complete ZrO_2 transformation to tetragonal phase
- Higher results in amorphous (or nano-crystalline) MnO_2 coverage not effectively utilized, expected SCR durability implications as well

Conditions:
320 ppm NO, 14% O_2, 2.5% H_2O, Balance of N_2, SV=300 L/g-hr



EPR shows activity correlation to Mn(II)

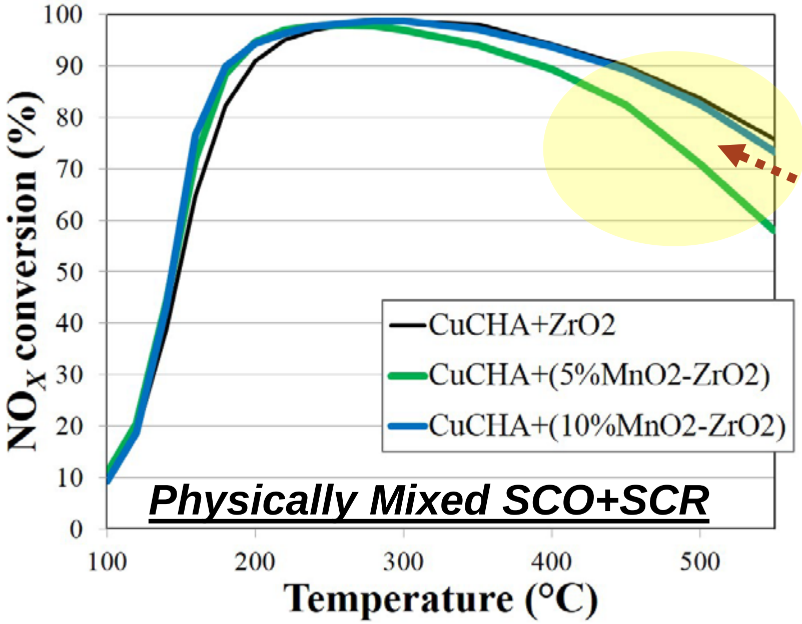
See back-up slides

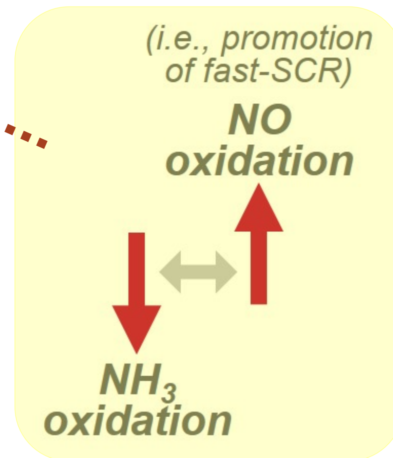


* High conversion likely having impact, thus not a true differential TOF result

Accomplishments

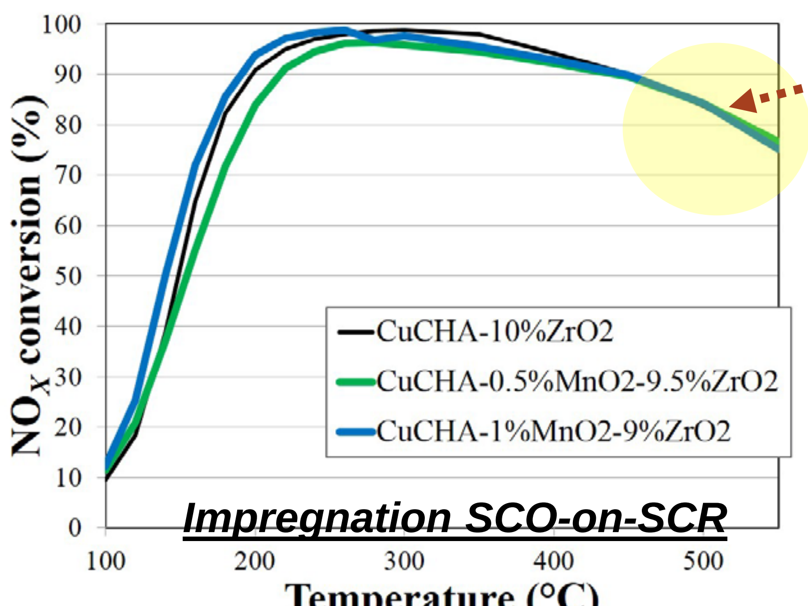
Method of SCO/SCR phase integration shown to impact both low & high temperature performance

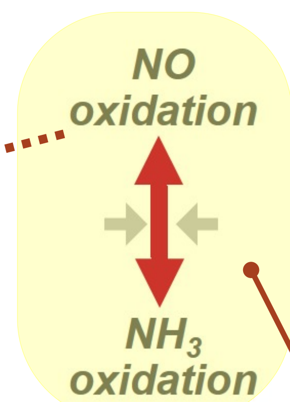




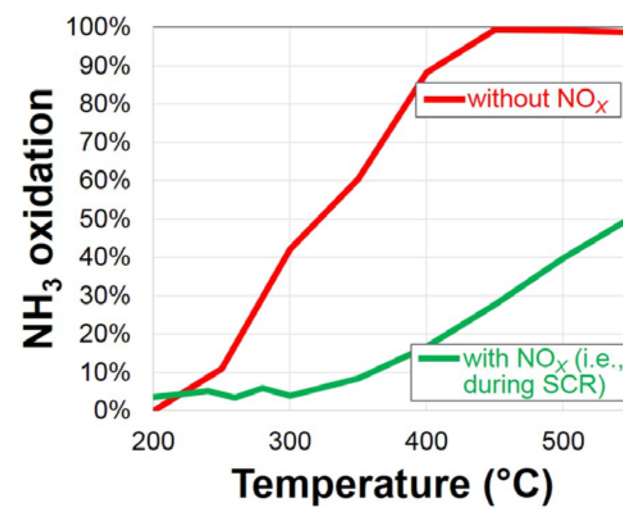
High temperature performance elucidates dual site interaction governed by relative proximity of active sites to each other

- Physical mixing = further proximity
- Impregnation = closer proximity



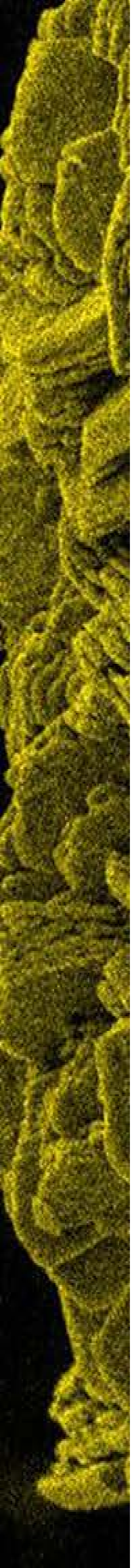


Similar effect as suppression of NH_3 oxidation under SCR reaction conditions



Accomplishments

SCO phase shown to promote fast-SCR

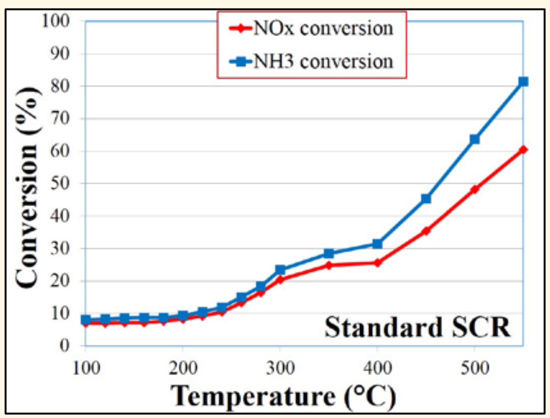


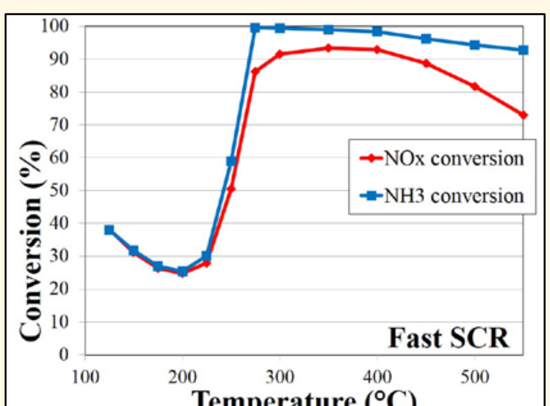
10% SCO / 90% SCR physically mixed
SCO = 10% MnO_2 / 90% ZrO_2 impregnated

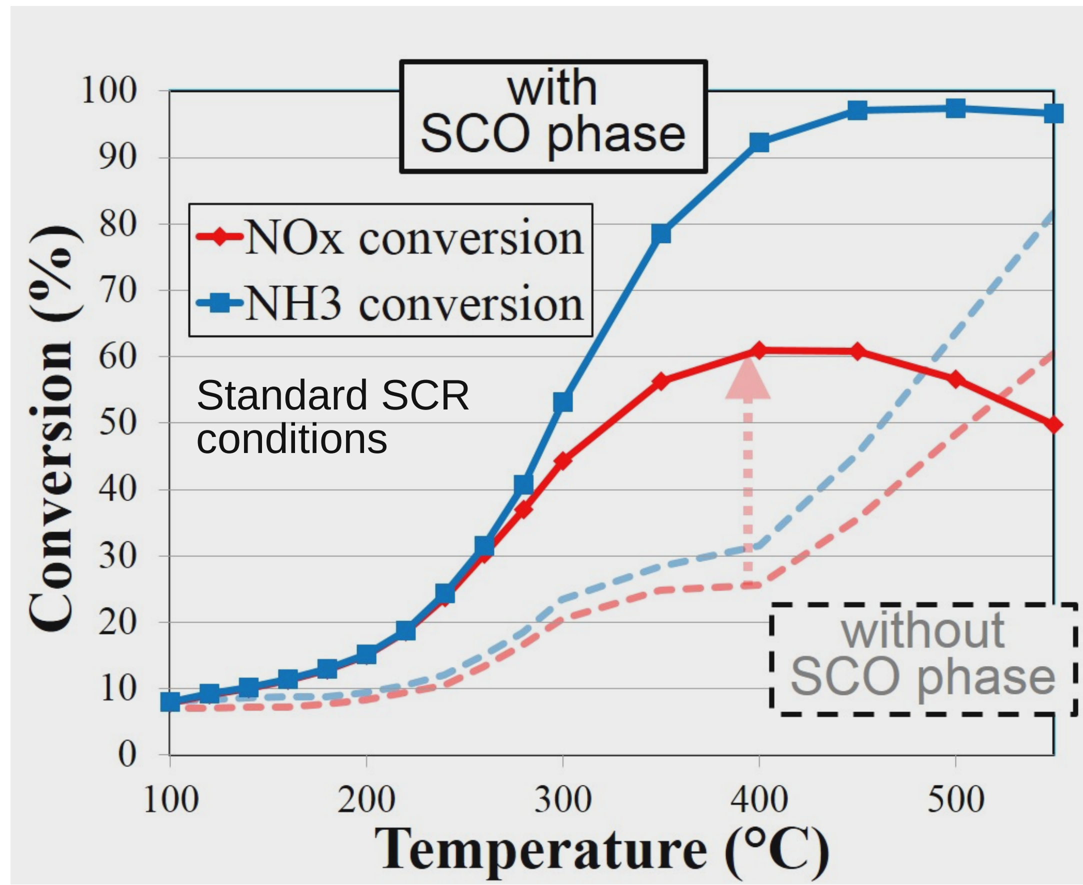
Conditions:
360 ppm NO, 360 ppm NH_3,
14% O_2, 2.5% H_2O,
Balance N_2, SV=300 L/g-hr

Without Cu, H-form SSZ-13 does not promote std-SCR but does promote fast-SCR

H-SSZ-13
(i.e., no Cu)





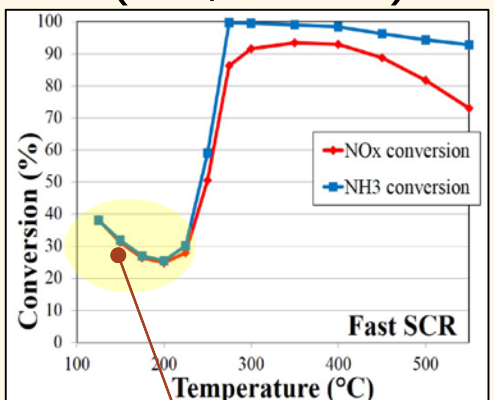


SCO phase with SCR shown to promote in-situ fast-SCR under standard-SCR conditions

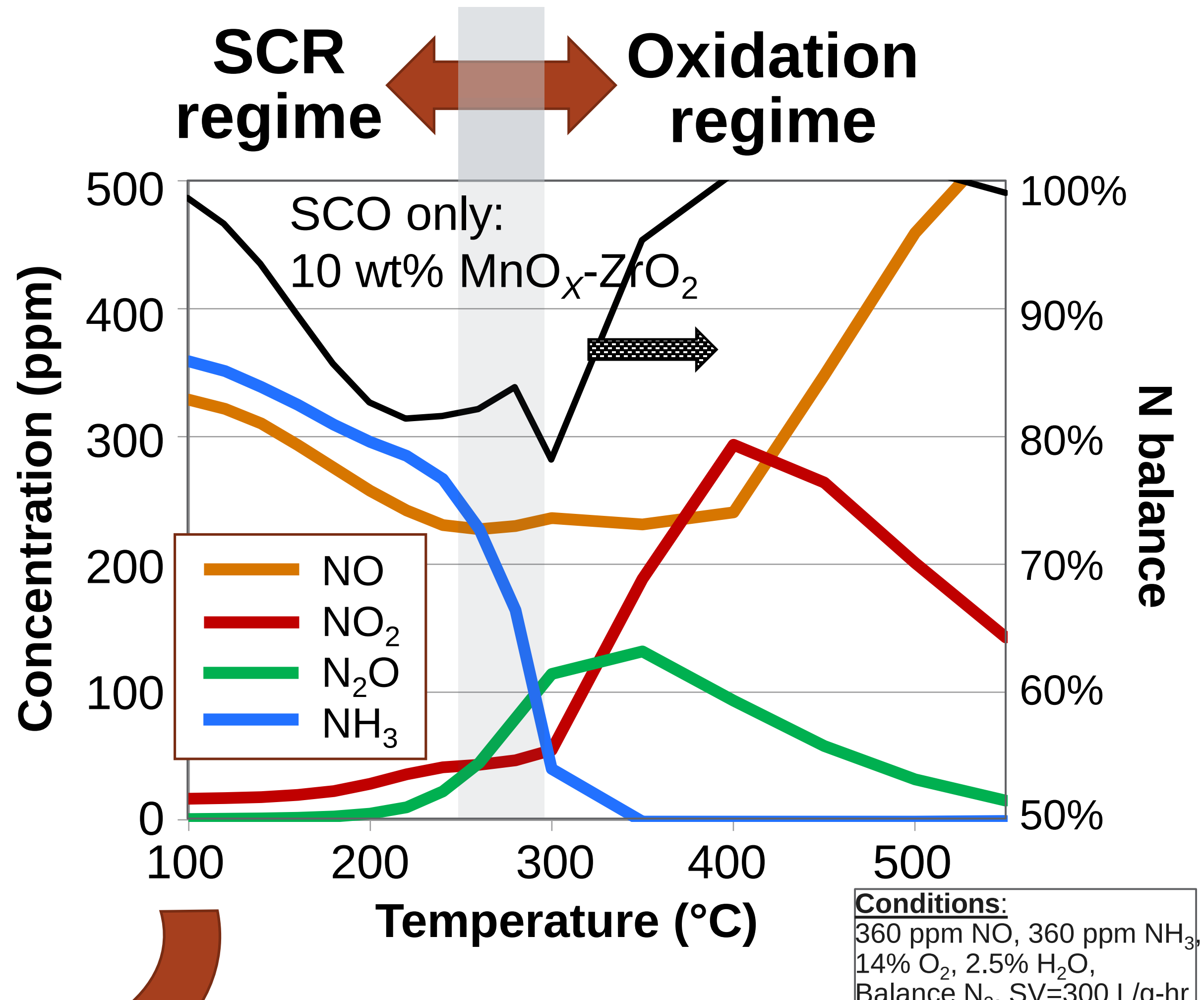
Accomplishments

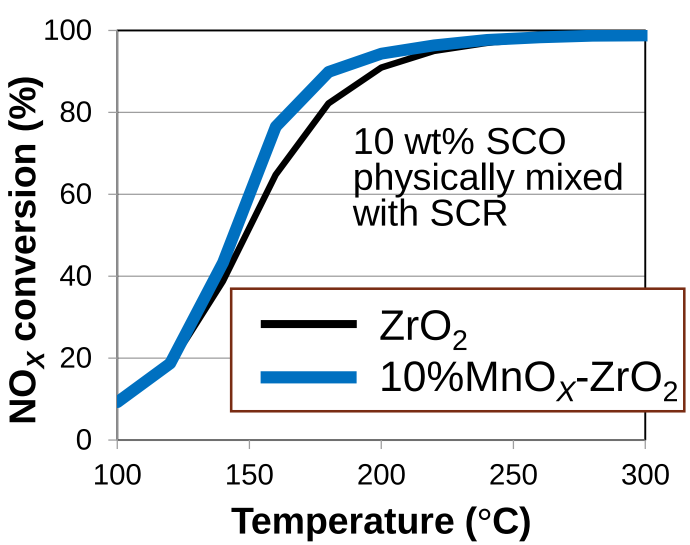
SCO phase shown to have bi-functionality demonstrating both SCR and oxidation regimes

H-SSZ-13
(i.e., no Cu)

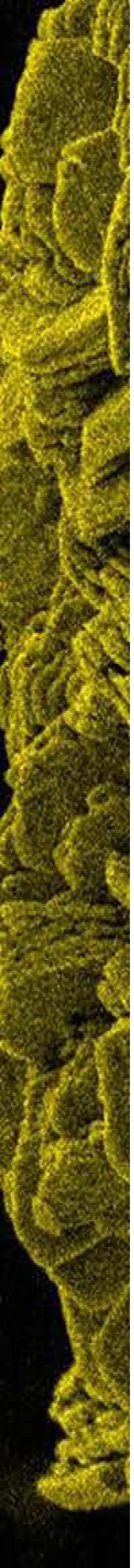


Not promoted
Nitrate formation





SCO phase exhibits low-temperature SCR while promoting higher temperature oxidation function



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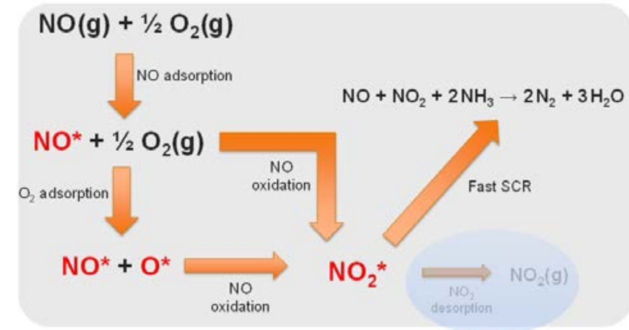
Accomplishments

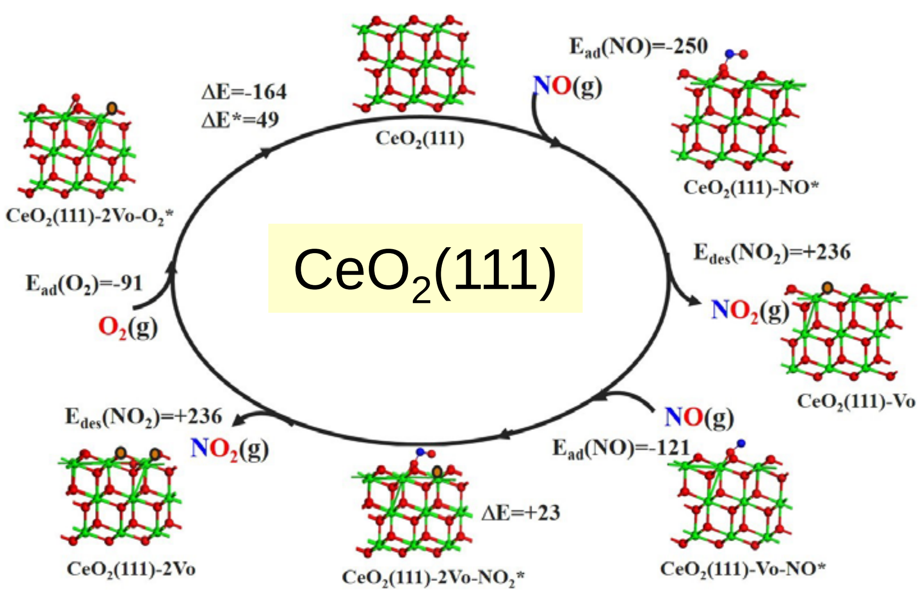
DFT modeling: the role of a surface-active intermediate

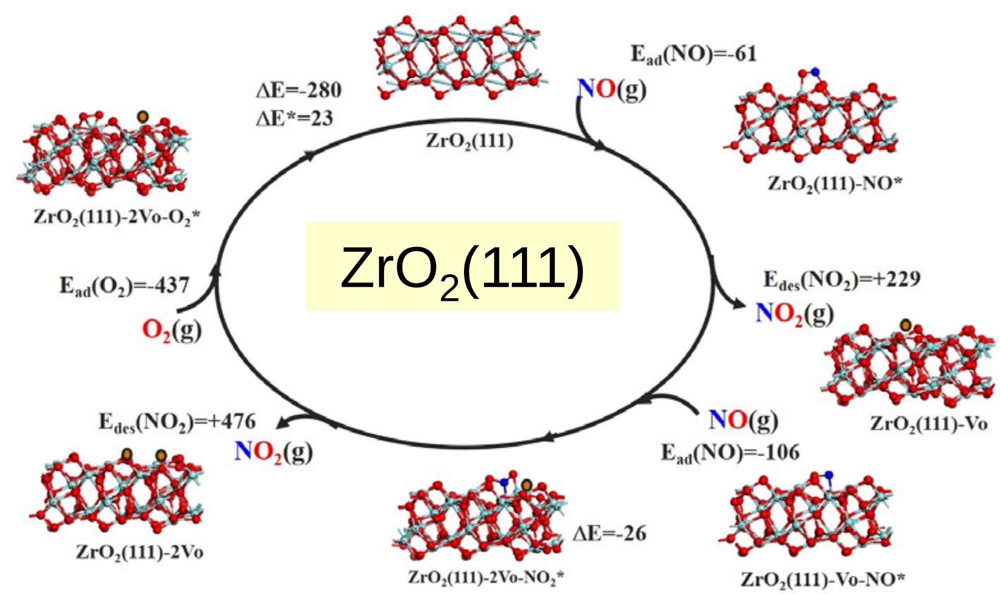
- Last year – Surface-active species contributing to fast-SCR
- i.e., <u>not subject to rate limitation by NO_2 desorption</u>
  - Supported by other groups, e.g., Grunert [Appl Catal B 182 (2016) 213-219]
  - E. Tronconi: HNO_2 considered to be critical intermediate [Top Catal 56 (2013) 109-113]



DFT modeling supports observation of fast SCR promotion without requiring NO oxidation enhancement

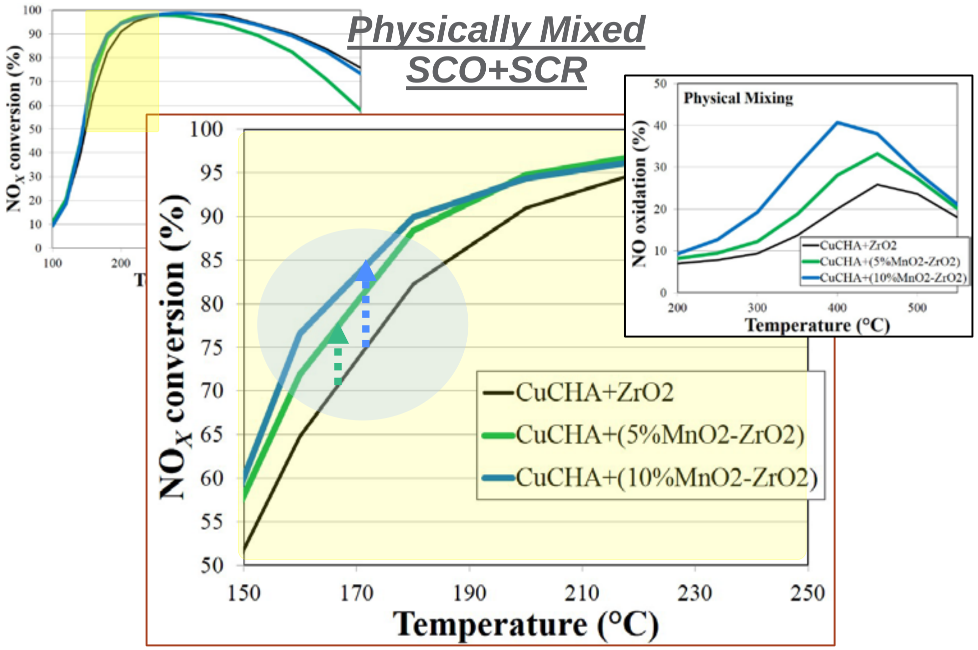
- NO_2 desorption rate-determining in NO oxidation over CeO_2(111) and ZrO_2(111) surfaces
- Will likely require close vicinity of SCO & SCR phases

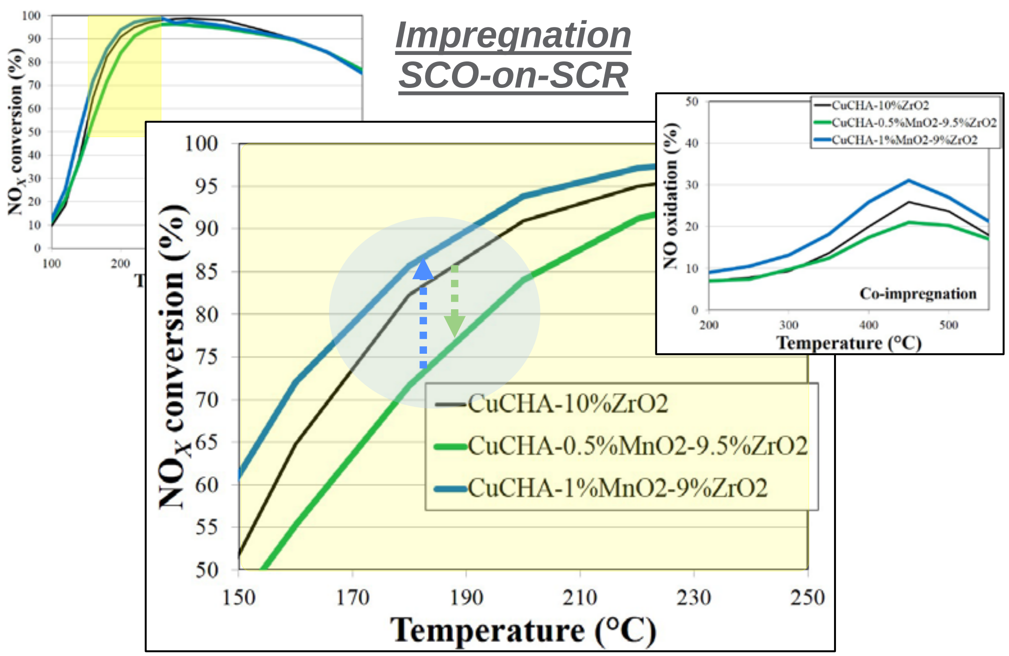




Accomplishments

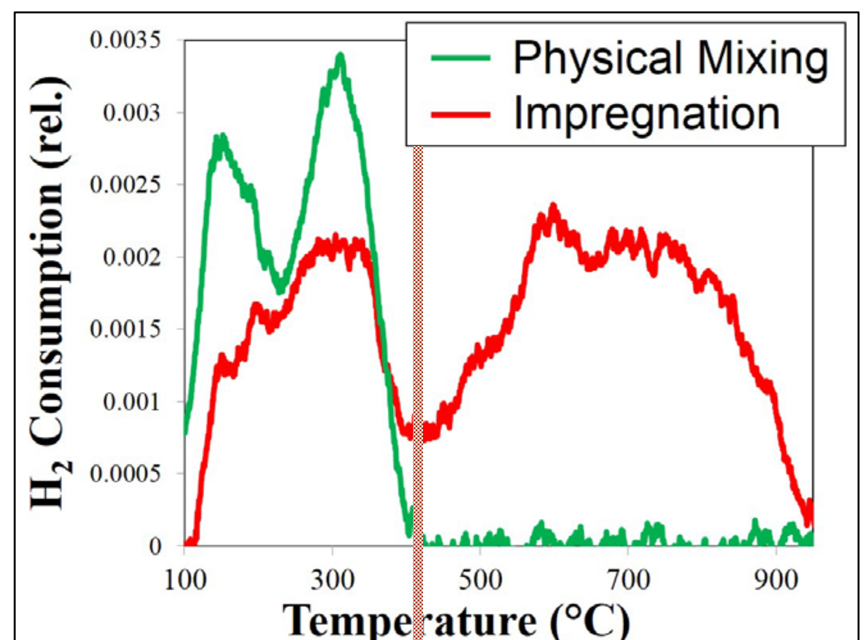
Method of SCO/SCR phase integration is shown to impact both the low & high temperature performance





Closer proximity of SCO & SCR phases occurs with a price

- Impregnation → a portion of the Mn is introduced inside zeolite
- Either displaces Cu or imparts a shadow effect
- Depression in SCR at low SCO loading



SCO-phase Mn

Ion-exchanged Mn

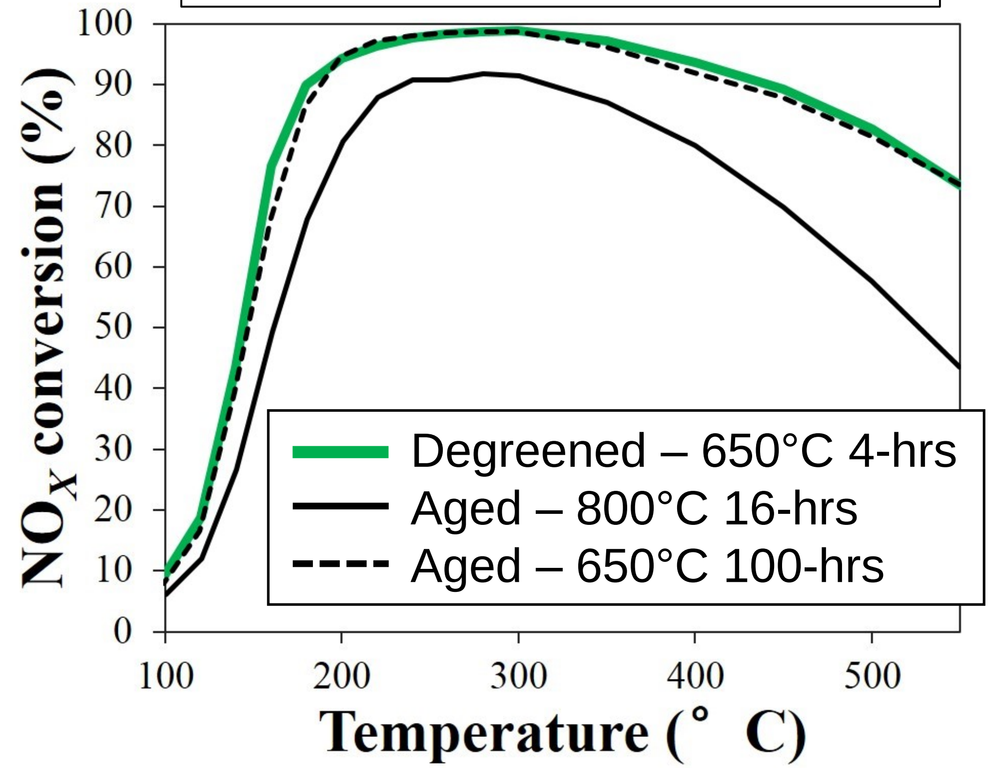
Accomplishments

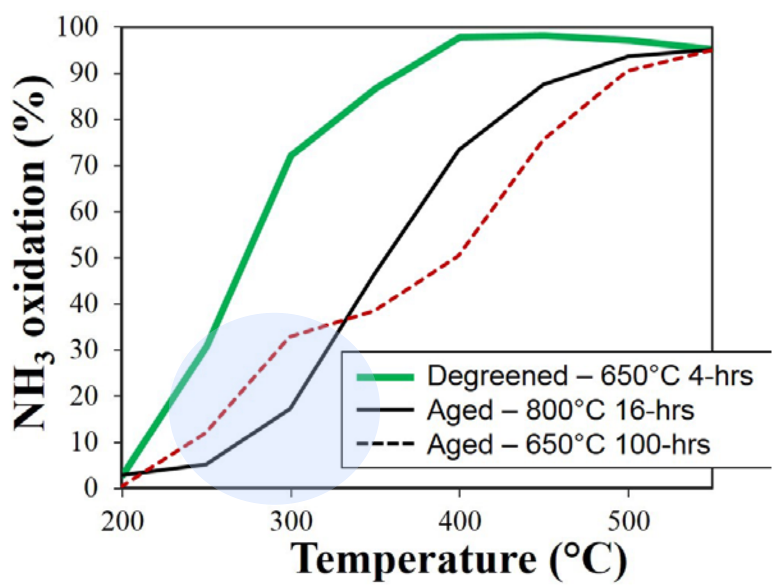
SCO-SCR phase interaction(s) result in multiple aging pathways feasible in the binary catalyst

Results demonstrate importance of realistic conditions for accurately predicting SCO-SCR aging and phase interaction(s)

- 800°C 16 hours – Significant SCR deactivation
- 650°C 100 hours – Little observed effect

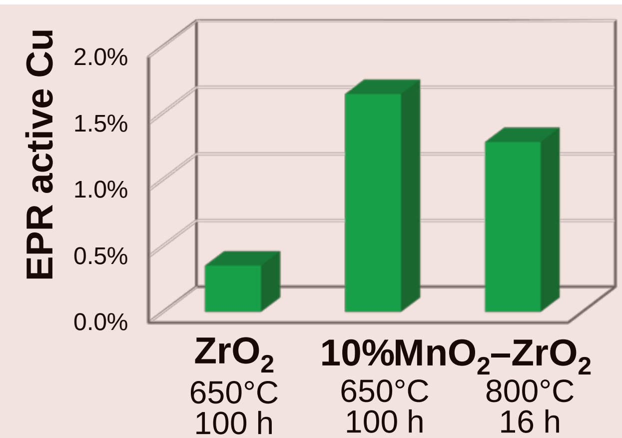
10% SCO / 90% SCR physically mixed
SCO = 10% MnO_2 / 90% ZrO_2 impregnated





NH_3 oxidation → 800°C 16 hours shows significant Cu active site degradation

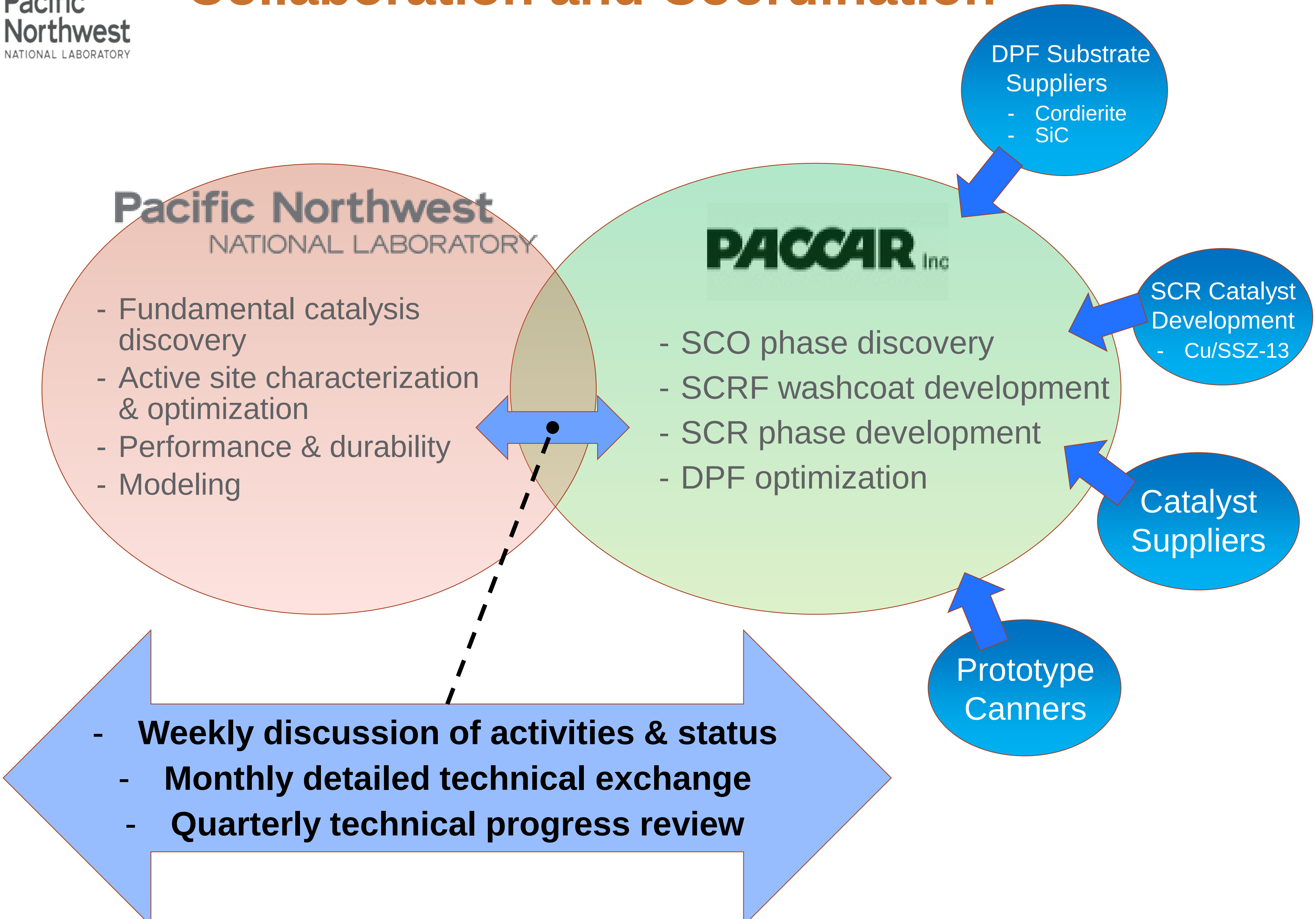
- Results suggest that Mn imparts a shift in $Cu^{2+} \leftrightarrow Cu(OH)^{+}$
- Impacts low-temperature performance



Responses to Reviewer Comments

Comment	Response
While increased NO_2 is a necessary condition for soot removal, it is not sufficient as also temperature and NH_3 play key roles, amongst other factors.	As discussed in Relevance/Approach, the biggest challenge with SCR-on-DPF for HD is the fast-SCR sink. This creates a diffusive-driven area void of NO_2 that penetrates upstream and encompasses soot as well. Hopefully in the Approach, a convincing argument has been made that that this is a catalysis challenge, and PNNL's focus & role. PACCAR is tasked with the systems-level view.
Low-temperature (activity) seems to face some issues, which would be one of the major issues to meeting standards, specifically the cold FTP cycle.	Significant discussion in Accomplishments highlights the low-temperature activity of the binary catalyst system as a means to assess (i) NO_2 formation in-situ on the catalyst, and (ii) aging of the system.
The reviewer questioned the plausibility of modifying … catalyst formulations to generate more NO_2. NO_2 generated from the SCR catalyst would require back diffusion of NO_2.	Back-diffusion of NO_2 is not required. The approach is to minimize the dependency of fast-SCR on *incoming* NO_2. By doing so, the magnitude of the NO_2-sink is reduced, thus reducing the magnitude & penetration of the diffusively-driven area void of NO_2.

Collaboration and Coordination



Remaining Challenges & Barriers

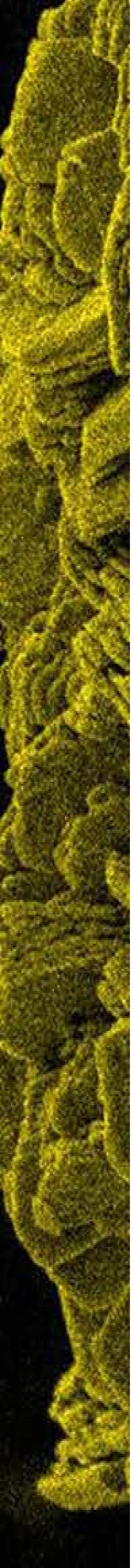
- Model-development that has with utility, to use for informed engineering of the binary catalyst-based SCRF system
  - This is on-going
  - To inform on SCO:SCR phase ratio design, capture fast-SCR promotion by SCO, accurately relate back to passive soot oxidation.
- Achieve ideal SCO:SCR phase integration …
- Identify ideal SCO:SCR design, including necessary phase ratio, implications to system performance & behavior (e.g., selectivity, durability)
- Sulfur sensitivity, desulfation requirements.

Proposed Future Research

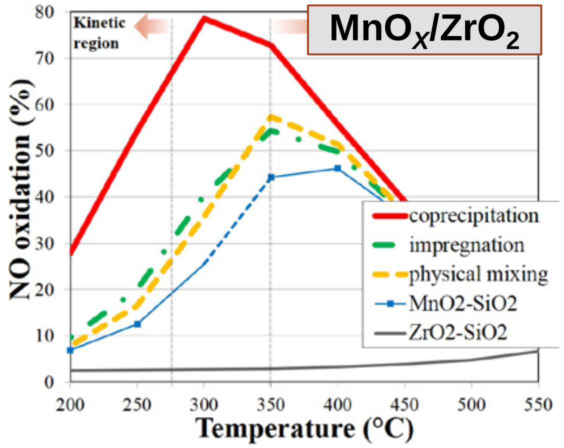
- Complete model development & validation for SCR-on-DPF reactor with binary catalyst system
- Develop an informed understanding of SCO:SCR phase ratio design, and implications of the design to NO_2 management & soot oxidation, reaction selectivity (i.e., fate of NH_3), SCR durability, SCR function (e.g., low-temperature performance)
- Engineering – model-driven informed design to determine the necessary SCO:SCR phase ratio and SCRF catalyst loading that:
  - Exhibits sufficient total in-situ NO_2 production …
  - to achieve acceptable passive soot oxidation performance in SCRF application …
  - while retaining acceptable catalyst durability & SCR reaction selectivity.
- Chemical poisoning – characterize sulfur sensitivity & desulfation requirements of MnO_X/ZrO_2 solid solution, pursue pathways to address prohibitive interaction if present.

Summary

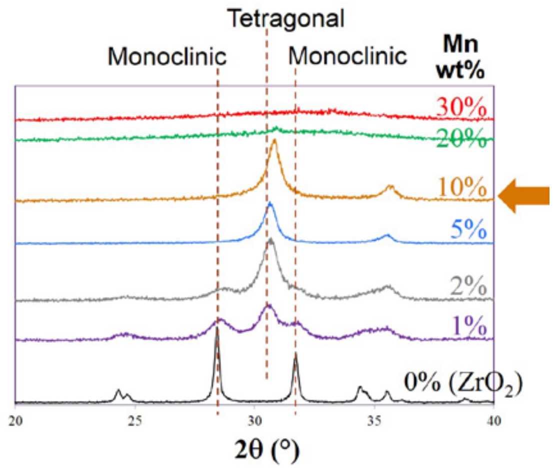
- Integrated SCR-on-DPF is a highly attractive exhaust aftertreatment architecture that can reduce cold start and SS emissions, but reduced passive soot oxidation that results requires an evolution to current state-of-the-art SCR catalyst technology for heavy-duty diesel to reduced fast -SCR functional dependence on incoming NO_2.
- An SCO phase made through co-precipitation of 10 wt% MnO_2 on ZrO_2 exhibits excellent NO oxidation activity achieved through (i) high Mn dispersion and maximized interface site density, (ii) complete ZrO_2 transformation to tetragonal phase, and without forming amorphous MnO_2 coverage.
- An optimized SCO phase is shown to exhibit bi-functionality providing low-temperature SCR function and medium- to high-temperature oxidation function for improved passive soot oxidation performance.
- The method of SCR and SCO catalyst phase integration and relative proximity of the active sites is shown to have impact on both high and low temperature performance, with close proximity attractive for reducing dependence on NO_2 desorption but incurring a cost of Mn going into the SCR zeolite framework.
- SCO-SCR phase interaction(s) result in multiple aging pathways feasible in the binary catalyst, and results emphasize the importance of realistic conditions for accurately predicting SCO-SCR aging



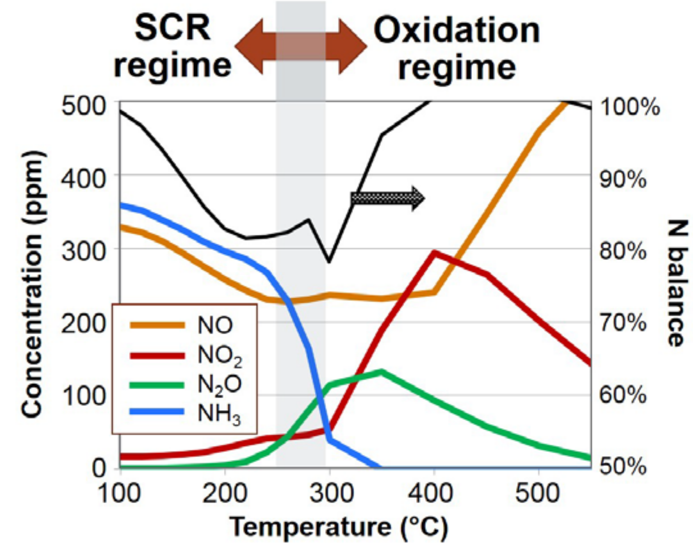
Summary



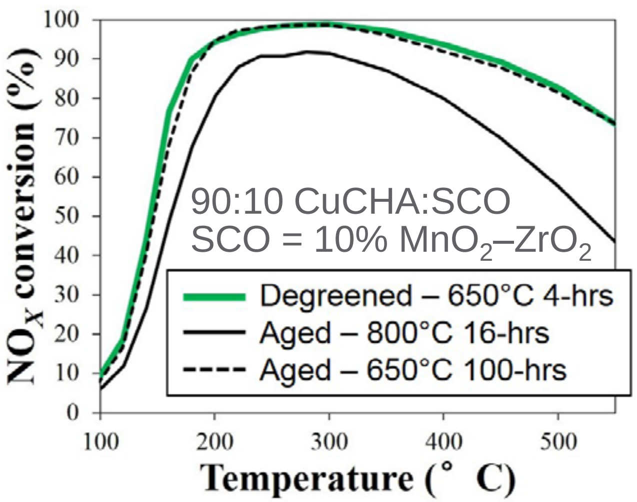
MnO$_X$/ZrO$_2$
Kinetic region
NO oxidation (%)
Temperature (°C)
coprecipitation
impregnation
physical mixing
MnO2-SiO2
ZrO2-SiO2



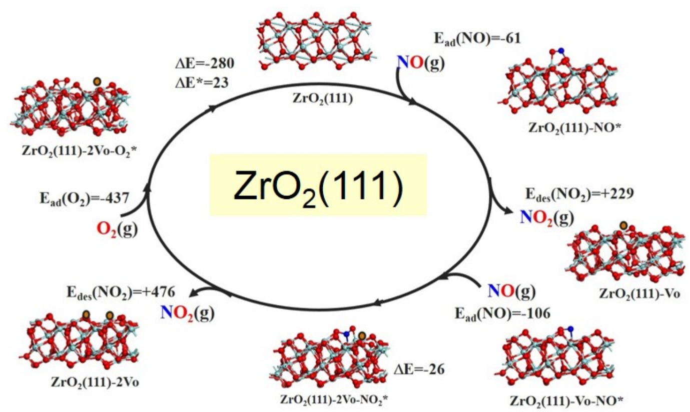
Tetragonal
Monoclinic
Monoclinic
Mn wt%
30%
20%
10%
5%
2%
1%
0% (ZrO$_2$)
2θ (°)



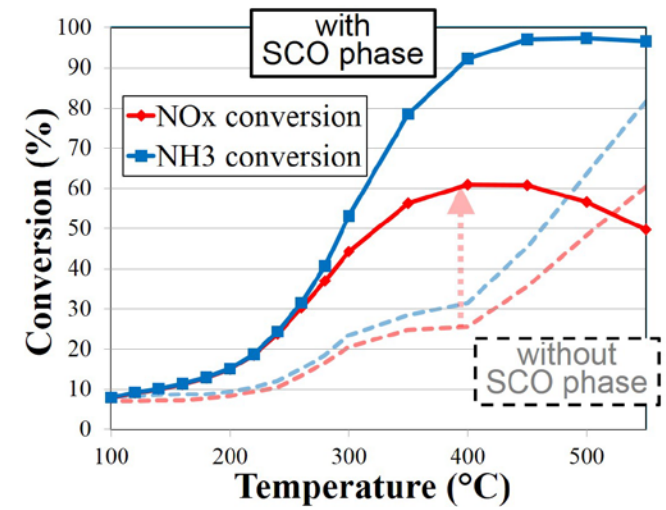
SCR regime
Oxidation regime
Concentration (ppm)
N balance
NO
NO$_2$
N$_2$O
NH$_3$
Temperature (°C)



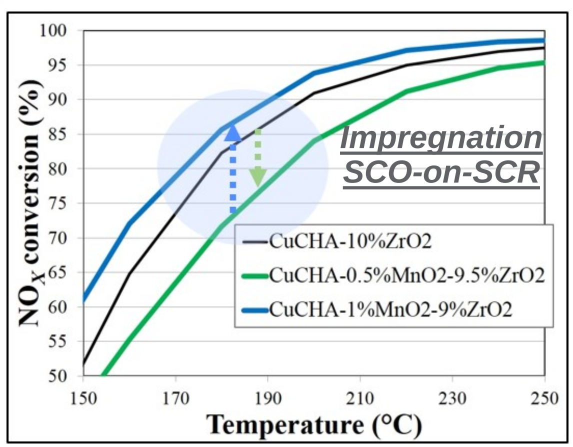
NO$_X$ conversion (%)
90:10 CuCHA:SCO
SCO = 10% MnO$_2$–ZrO$_2$
Degreened – 650°C 4-hrs
Aged – 800°C 16-hrs
Aged – 650°C 100-hrs
Temperature (° C)



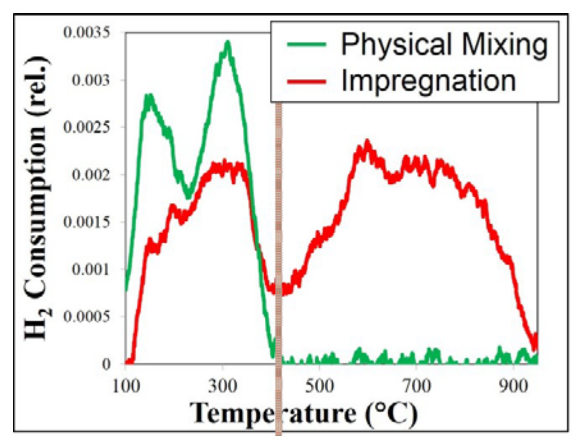
ZrO$_2$(111)
ΔE=-280
ΔE*=23
ZrO$_2$(111)
E$_{ad}$(NO)=-61
NO(g)
ZrO$_2$(111)-NO*
ZrO$_2$(111)-2Vo-O$_2$*
E$_{ad}$(O$_2$)=-437
O$_2$(g)
E$_{des}$(NO$_2$)=+229
NO$_2$(g)
ZrO$_2$(111)-Vo
E$_{des}$(NO$_2$)=+476
NO$_2$(g)
ZrO$_2$(111)-2Vo
NO(g)
E$_{ad}$(NO)=-106
ΔE=-26
ZrO$_2$(111)-2Vo-NO$_2$*
ZrO$_2$(111)-Vo-NO*



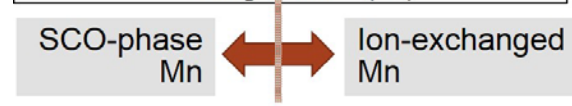
with SCO phase
NOx conversion
NH3 conversion
without SCO phase
Conversion (%)
Temperature (°C)



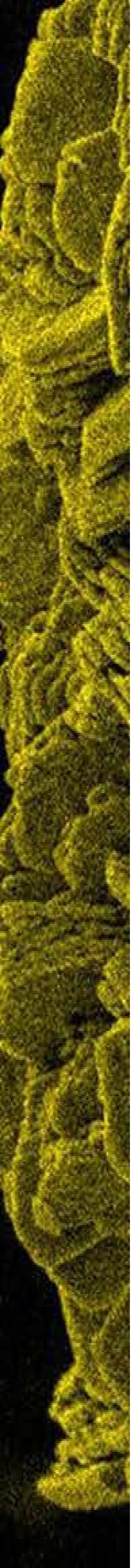
NO$_X$ conversion (%)
Impregnation SCO-on-SCR
CuCHA-10%ZrO2
CuCHA-0.5%MnO2-9.5%ZrO2
CuCHA-1%MnO2-9%ZrO2
Temperature (°C)



Physical Mixing
Impregnation
H$_2$ Consumption (rel.)
Temperature (°C)



SCO-phase Mn
Ion-exchanged Mn



Thank you